Uncertainty Analysis for the Parameterization of Glycols

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Uncertainty Analysis for the Parameterization of Glycols

A review of the 4C association scheme for mono-ethylene glycol (MEG)

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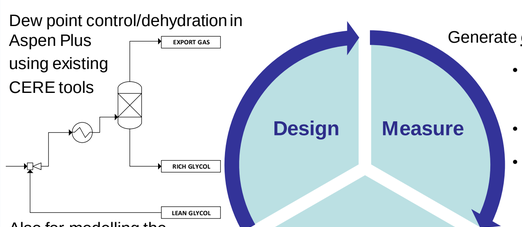
Background

- Collaboration between DTU-CERE and Statoil ASA
- Natural gas dehydration: Statoil Subsea Factory™(1) and Gas-2-Pipe™(2)
- Important Sales Gas specifications:
  - Hydrocarbon dew point: cricondenbar 105-110 bar
  - H_2O dew point: 32 ppm
  - Glycol in the gas phase 8 l/MSm^3

Phase equilibria **measurements** and thermodynamic **modelling** of petroleum fluids relevant to **subsea processing**



Generate **experimental data**:

- CH_4 – MEG/TEG – H_2O
  - Focus on vapour phase
- Temperature: 10 – 70 ° C
- Pressure: 30 – 150 bar

- **Modelling** of the experimental data with **CPA**
- New considerations for MEG within the association framework e.g. new parameter sets, k_{ij} and association schemes

Figure 1: Planned workflow for the Subsea Processing Project

Literature Review

CPA parameterization of glycols

- CPA(3) parameter sets(4) for glycols fitted to pure component DIPPR(5) correlations, with liquid-liquid equilibrium (LLE) selection criterion

Uncertainty analysis utilized in CPA model development

- Bootstrapping recently used(6) to for CPA parameter estimation of CO_2
- Effect of using pseudo data was not specifically evaluated

Literature survey: data for systems of interest

- Binary data are relatively scarce in the open literature and often incongruent
- Single ternary data set (methane-water-MEG) available(7)
- CPA can model both phases (mixture parameters fitted CH_4 solubility data only)

Methodology

Parameter evaluation and uncertainty analysis

1. Data selection: pure and multicomponent
2. Determine objective function for parameter estimation:

$$OF_{\min}\left(a_0, b_0, c_1, \frac{\varepsilon}{R}, \beta, k_{ij}\right) = w_i \sum \left| \frac{i_{calc} - i_{\exp}}{i_{\exp}} \right|^2$$

$$\mathrm{i} \in [\mathrm{P_{Sat}}, \rho, \mathrm{TPx}, \mathrm{TPy}]$$

3. Run optimization to obtain new parameters
4. Bootstrap: randomly sample (with replacement) from experimental data and refit parameters according to OF_{min}
5. Repeat Step #4 1500 times
6. Determine parameter distributions and confidence intervals
7. Evaluate performance versus literature

Results and Discussion

Use of pure component experimental data versus pseudo data

- Accuracy of MEG liquid density prediction sacrificed by incorporating the LLE-criterion
- MEG vapour pressure data exhibits significantly higher variance than the DIPPR correlation suggests
- Bootstrapped parameter plots show high degree of correlation when fitting to DIPPR

Uncertainty analysis: new CPA-4C MEG parameters

- Literature parameters do not match well with bootstrapped mean parameter estimator
- Mean of the average absolute error and 95% confidence interval over 1500 optimization runs:

Table 1: Parameter confidence intervals and fitting errors for newly proposed MEG 4C parameters

	Parameter							Data fit error [% ARD]				
	b_0 [cm^3/mol]	Γ [K]	c_1	ε/R [K]	β 10^3	k_{12}	k_{13}	P_{Sat}	ρ	TPx_{12}	TPx_{13}	TPy_{13}
Literature	51.40	2532	0.6744	2376	14.10	-0.105	0.1786 0.1340	1.96	2.44	4.80	5.51 17.2	35.1 28.8
This work*	50.22	2830	0.6804	2197	14.74	-0.1233	0.093					
95% CI (lb)*	50.13	2827	0.6738	2183	14.71	-0.1283	0.087	**1.78**	**0.81**	**3.01**	**4.55**	**15.4**
95% CI (ub)*	50.41	2849	0.6819	2198	14.82	-0.1215	0.094					

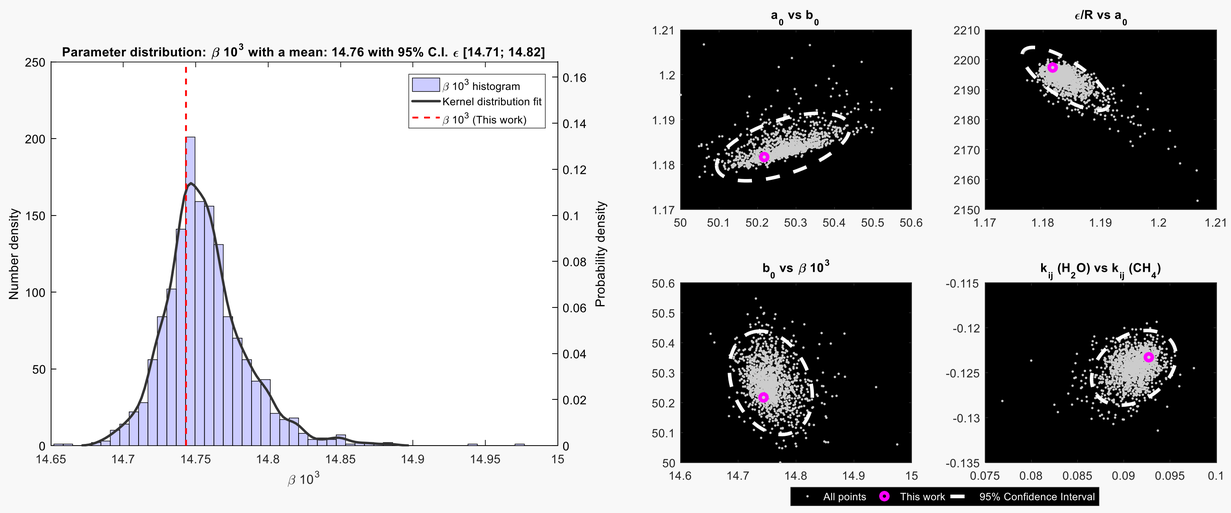


Figure 2: Selected parameter distribution (left) and correlation plots (right), showing confidence intervals developed from the bootstrap method

Application for Simplified NG Dehydration Systems

Binary systems

- Improved correlation of the MEG entrained into CH_4-rich phase
- Prediction is best at both high temperature and high pressure
- Low temperature anomalies may be due to experimental difficulties

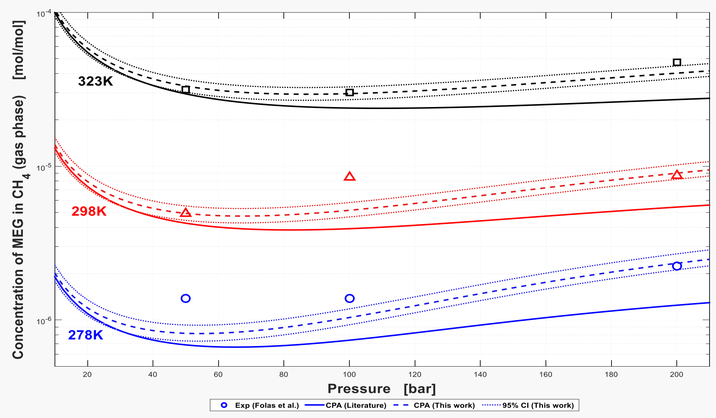


Figure 3: Correlation of MEG vapour phase fraction in CH_4

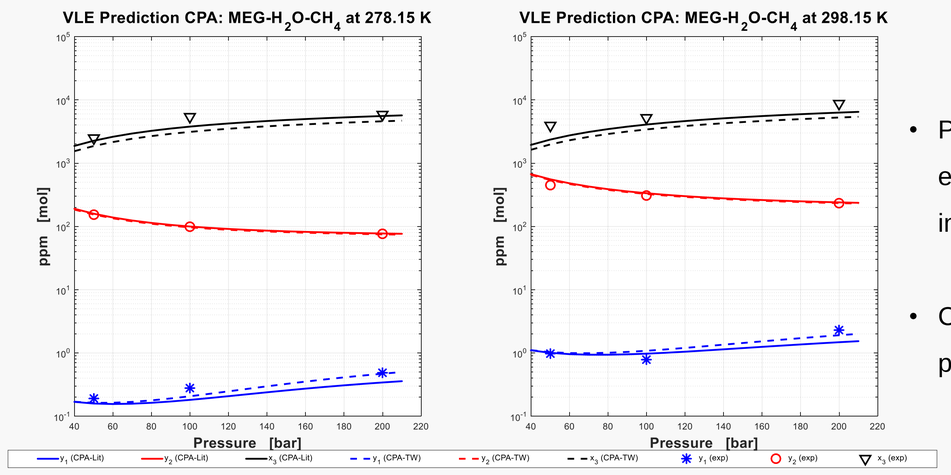


Figure 4: Ternary VLE predictions for MEG-H_2O-CH_4 at 278K and 298K

Ternary systems

- Prediction for MEG entrainment is much improved
- CH_4 solubility in the liquid phase is underpredicted

Conclusions

- Excess (unnoticed) parameter correlation avoided by using raw experimental data in optimization routines
- New MEG 4C parameters provide improved description for simplified natural gas dehydration applications
- Accurate prediction of all components in all phases remains challenging
- Discrepancies highlight need for further experimental data and model development

Future Work

- Generation of new experimental data for additional model evaluation
- Apply uncertainty analysis to newly proposed association schemes
- Inclusion of tri-ethylene glycol (TEG) data and modelling
- Modelling of natural gas dehydration in Aspen

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CERE
Center for Energy Resources Engineering

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